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Journal of Alloys and Compounds 463 (2008) 1–5

Journal of ALLOYS AND COMPOUNDS

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Molecular H_2 trapped in AlH_3 solid

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Received 30 July 2007; received in revised form 23 August 2007; accepted 27 August 2007
Available online 1 September 2007

Abstract

Solid aluminum hydride, AlH_3, has been proposed and studied for applications in hydrogen storage. In some samples, a comparatively narrow feature in the proton NMR spectrum is observed; we demonstrate here that this peak is due to molecular hydrogen (H_2) trapped within the solid, presumably from earlier processing procedures or partial decomposition. Static and magic-angle spinning NMR show that the responsible species is highly mobile, even at 11 K. Neutron-energy-gain spectra obtained at 3.5 K yield a feature at or near the free-rotor H_2 energy difference between the $J=1$ and $J=0$ states. Both NMR and neutron scattering demonstrate *ortho–para* conversion at low temperatures. Similar NMR signatures in other hydrogen-storage solids such as $NaAlH_4$ may also be due to trapped H_2.

Keywords: Hydrogen-storage materials; Magnetic measurements; Neutron scattering; Nuclear resonances

1. Introduction

Aluminum hydride (AlH_3) has been discussed and studied recently for hydrogen-storage applications [1–3]. Depending on preparation conditions, several AlH_3 polymorphs with different structures can be produced, where the most stable polymorph is denoted as the α-phase [4]. These hydrides can decompose into aluminum metal and hydrogen gas:

$$AlH_3 \rightarrow Al + \frac{3}{2}H_2, \quad (1)$$

yielding 10% of the initial mass as hydrogen gas. While the large hydrogen content is attractive, these AlH_3 phases cannot be regenerated simply by putting an overpressure of H_2 above the Al metal reaction product unless extremely high pressure is used [1]. Thus, this system would require off-vehicle regeneration.

We note that reaction (1) is very weakly endothermic [5]; thermodynamically, the reaction will drive in the indicated direction (dehydriding) unless H_2 pressures of order 10^5 bar are present. Hence, the observation that AlH_3 solid does not rapidly decompose at room temperature must result from kinetic inhibition. Heating to 100–150 °C does produce rapid decomposition [1–3,5].

Proton NMR spectra of some samples of AlH_3 reveal a motionally narrowed component, in sharp contrast to the rigid, dipolar-broadened spectrum of the solid AlH_3 component. Indeed, Zogal et al. reported such a feature in spectra produced by both continuous-wave [6] and pulsed [7] methods years ago, which they attributed to molecular hydrogen (H_2) adsorbed on surfaces of the hydride particles [7]. Similar narrow NMR components have been reported [8–14] in related hydrogen-storage systems such as $NaAlH_4$. Here we present proton NMR spectra obtained over a broad temperature range and neutron-energy-gain spectra at 3.5 K. Together, they conclusively demonstrate that the motionally narrowed signal is from H_2 trapped in the AlH_3 solid,

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doi:10.1016/j.jallcom.2007.08.071

presumably during earlier processing or from partial decomposition.

2. Description of samples

Aluminum hydride from two sources was used in these studies. First, "Dow/BNL" material was obtained through J. Graetz and J.J. Reilly of Brookhaven National Laboratory (BNL). It had been originally prepared at the Dow Chemical Company as described by Brower et al. [4] as a possible component in solid propellants for rocket motors and had been stored at BNL for approximately 30 years [1,15]. The second material was "Russian/UTRC" and had been originally obtained from an unspecified Russian source by United Technologies Research Center (UTRC) and provided to the Jet Propulsion Laboratory (JPL) for NMR characterizations [16]. No further information on the provenance of this material is available. At JPL and Caltech, both materials were stored under argon; at WU and NIST, a dry N_2 atmosphere was used. We note that the Dow material was probably exposed to air during most of its 30-year storage.

X-ray diffraction was used at JPL to confirm the identity of each material as α-phase AlH_3 [17], while ^{27}Al NMR spectra indicated each also contained a small amount of Al metal [15,16]. SEM micrographs [3] showed that the Dow/BNL material was in the form of cubes of roughly 50–100 μm length on a side, with many tunnels or small holes showing on each face as illustrated in Fig. 1(a). The most prominent openings are of order 5 μm in diameter; there are probably numerous smaller ones that are too small to resolve. In contrast, the SEM image in Fig. 1(b) for the Russian/UTRC powder reveals smaller and more symmetric particles with mostly smooth surfaces. Hence, the morphologies and, presumably, microstructures reflect significant differences from the preparation and processing treatments used during the synthesis of these different batches of α-phase AlH_3. There was no evidence of surface coatings from either ^{13}C NMR or IR spectroscopy; in the Dow/BNL sample, ^{27}Al solid-state NMR indicated the presence of aluminum oxides [15,16].

3. Results and discussion

Static proton NMR spectra of the Dow/BNL sample of AlH_3 appear in Fig. 2. The sample was loaded into the magic-angle spinning (MAS) probe of a Bruker DSL-500 spectrometer [18] operating at 11.7 T, but with the spinning gas off. At a recycle delay of 300 s, a signal from the rigid solid (approximately 65 kHz FWHM) and a narrow signal appear. At 1 s recycle delay, the solid AlH_3 signal is absent while the narrow signal remains at the same intensity. Both the narrowness of the line and its short relaxation time T_1 demonstrate that the sharp signal is from a mobile species (i.e., rapidly rotating and, possibly, translationally mobile). From the relative peak areas of the narrow-to-broad components in fully relaxed spectra, it was estimated that ~3.2% of the total proton content contributes to the sharp peak [15]. Similar measurements on the Russian/UTRC sample show essentially no evidence for the sharp resonance

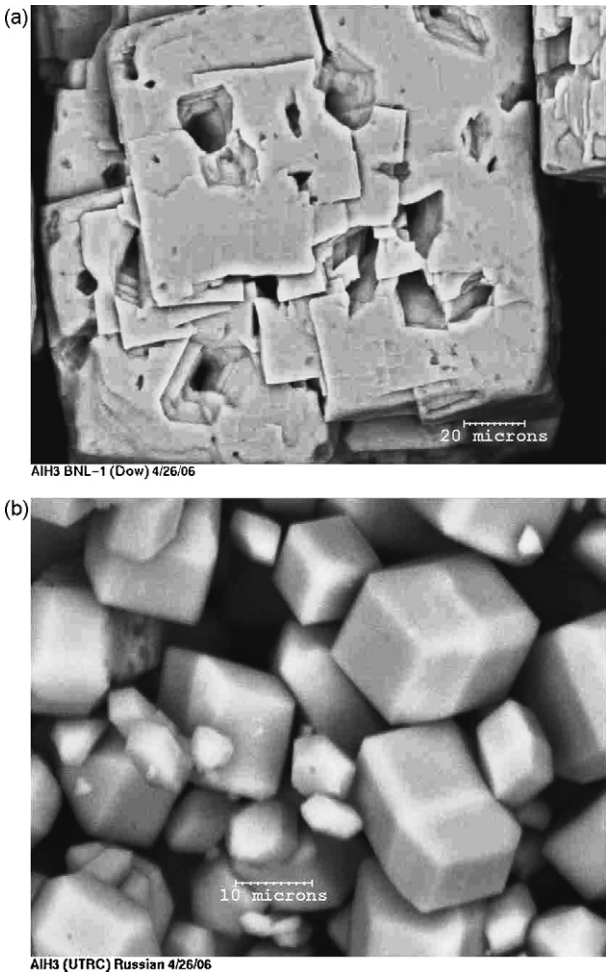

Fig. 1. Scanning electron microscopy (SEM) images of alane particles. (a) Prepared originally at Dow Chemical Company and provided by Brookhaven National Laboratory (BNL) and (b) provided by United Technologies Research Center (UTRC) from an unspecified Russian source.

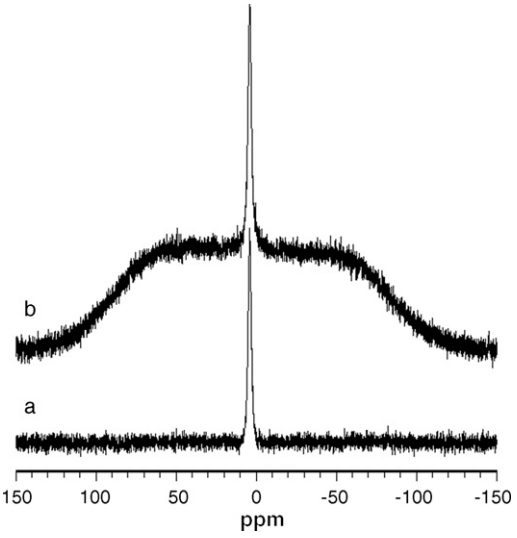

Fig. 2. Static proton NMR spectra at 500 MHz of the Dow/BNL AlH_3 sample at 293 K. The upper curve was obtained with a long recycle delay of 300 s, so the broad AlH_3 solid signal and the sharp H_2 signal were both well recovered. In the lower curve at 1 s recycle delay, the AlH_3 signal is suppressed (long T_1) while the H_2 signal remains (short T_1).

peak. Throughout this work, the sharp signal is labeled "H_2", identification which is proven below.

Magic-angle spinning NMR at rotational frequencies from 6 to 14 kHz yields further narrowing of the sharp "H_2" signal, but little narrowing of the broad AlH_3 signal [15]. The "H_2" peak is centered at 4.4 ppm relative to the standard reference compound tetramethylsilane (TMS) and has a FWHM of approximately 0.22 ppm. Variable-temperature MAS-NMR experiments show the peak to be present from the lowest temperature surveyed (i.e., 208 K) up to 423 K, where the sample decomposes rapidly [16]. The present 4.4 ppm shift value agrees with the chemical shift of 4.3–4.5 ppm for molecular H_2 (when referenced to TMS) as reported in several recent literature sources [19–21]. Almost all organic solvents would solidify (and their NMR lines broaden to nearly the width of the AlH_3) at 208 K; thus any solvents possibly used in the material synthesis are not likely sources of the sharp line. The persistence of the sharp signal to 423 K rules out adsorbed H_2 (indeed strong adsorption of H_2 even at room temperature is essentially unheard of); instead, the H_2 must be primarily trapped inside the material.

The Dow/BNL sample was moved to a variable-temperature dewar; proton NMR spectra are reported at 354 MHz in Fig. 3(a) at 77, 31, and 11 K. The "H_2" line remains much narrower than the signal from the AlH_3 solid over this temperature range, demonstrating the mobility of this species even at cryogenic temperatures. Over this range, the T_1 of the "H_2" signal remained

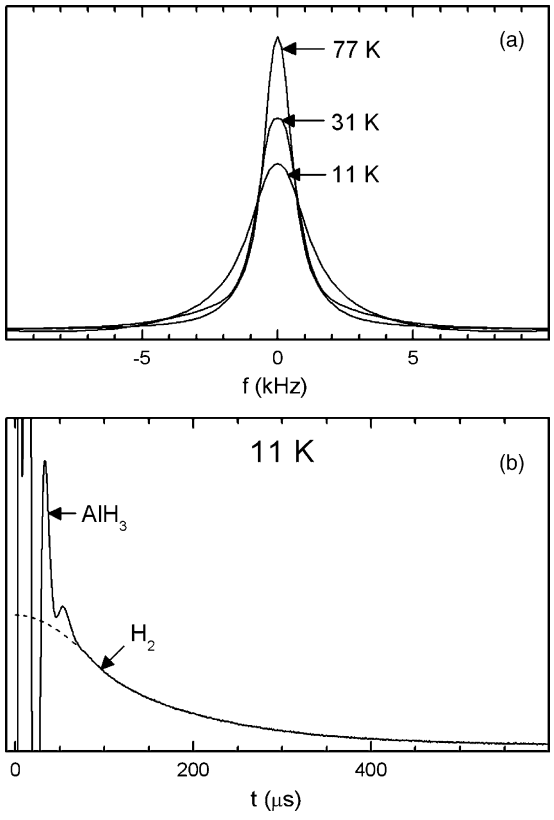

Fig. 3. Proton NMR (static) of the Dow/BNL AlH_3 sample at low temperatures and 354 MHz. (a) Frequency spectra of the narrow H_2 component at 77, 31, and 11 K. (b) The proton NMR FID; at early times, the (off-scale) rapidly decaying solid signal is evident. The H_2 signal is the component remaining after 70 μs.

below 0.2 s, an additional indication of high rotational mobility. These data are only consistent with molecular H_2. We note that bulk H_2 boils at 20.2 K and freezes [22] at 14 K; motional narrowing of the bulk solid H_2 NMR signal [23,24] from translational self-diffusion is apparent above 10 K.

Fig. 3(b) presents the time-domain signal at 11 K (FID, free induction decay) following a single $\pi/2$ rf pulse. The signal from solid AlH_3 is initially off-scale and shows oscillations (i.e., dipolar Lowe beats [25]). After 70 μs, the solid signal has fully decayed and only the "H_2" signal remains. At higher temperatures where the "H_2" spectrum is narrower, a clean distinction between the two signals is even more evident. Below 11 K, the frequency broadening of the "H_2" signal makes such an AlH_3 *versus* "H_2" distinction less clear.

In detail, the frequency spectra of Fig. 3(a) were obtained by eliminating the rapidly decaying AlH_3 solid signal from the FIDs by using a Gaussian extrapolation of the "H_2" FID signal back to zero time, with subsequent Fourier transformation. The "H_2" signal amplitude M was also monitored as a function of temperature, T; the product MT is expected to be constant (Curie law nuclear spin susceptibility). However, the experimental MT product gradually decreased by about a factor of three upon cooling to 20 K, suggesting that the rotational motion of some H_2 molecules froze-out at higher temperatures. Conversion of *ortho*-H_2 to *para*-H_2, as discussed below, may also be involved.

Molecular H_2 appears in two forms [22], *ortho*-H_2 with total nuclear spin $I = 1$ (two proton spins parallel) and molecular rotation quantum number $J = 1, 3, 5\ldots$, and *para*-H_2 with $I = 0$ (anti-parallel proton spins) and even values of J. The distinction is a result of the requirement that the overall molecular wavefunction invert in sign upon interchange of the identical hydrogen nuclei (Fermions). The energy of each state (unperturbed, as in the gas or liquid or even bulk H_2 solid) is

$$E = \left(\frac{\hbar^2}{2I}\right) J(J+1) = BJ(J+1), \tag{2}$$

where $B/k = 85.6$ K. The large value of B reflects the fact that H_2 has the shortest chemical bond length known and the lightest nuclear masses, providing a very small moment of inertia, I.

At low temperatures (below 25 K), thermal equilibrium would have essentially all H_2 as $J = 0$ *para*-H_2. However, conversion between *ortho* and *para* is very slow, requiring a magnetic field gradient (to cause a relative precession of the two proton spins) oscillating at the $J = 0$ to $J = 1$ frequency, $\Delta E/\hbar$. In solid H_2 at low temperatures, the magnetic field gradient is provided by a neighbor *ortho*-H_2. Thus the conversion follows bimolecular kinetics [22]:

$$\frac{dc}{dt} = -kc^2, \tag{3}$$

where c is the fraction of *ortho*-H_2 and k has been measured to be $0.019\ h^{-1}$.

Room-temperature proton NMR spectra of the Dow/BNL sample of AlH_3 appear in Fig. 4. The more intense spectrum was obtained before the sample was cooled, so the *ortho*-H_2 concentration c is 0.75, the high-temperature equilibrium value.

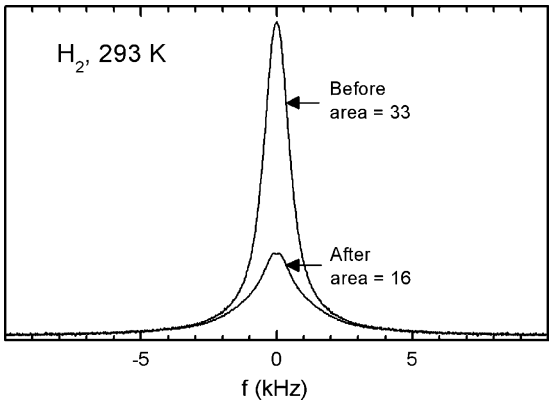

Fig. 4. Static proton NMR spectra at 293 K and 354 MHz, with only the narrow H_2 component shown. The higher curve is from the Dow/BNL AlH_3 sample before immersion in a liquid-helium storage dewar. The lower curve is from the same sample after 4 days at 4.2 K. The ratio of areas is 0.48; the smaller resonance has a somewhat greater linewidth.

After 4.0 days of immersion of the sample (in a sealed glass tube) in liquid-helium in a storage dewar, the sample tube was removed; the resulting NMR spectrum had approximately one-half the initial intensity (recall *para*-H_2 is $I=0$ and yields no NMR signals). The measurements in Fig. 4 were performed only after verifying that the NMR equipment's sensitivity was unchanged, using a second sample that always remained at room temperature. Integration of Eq. (3) yields

$$\frac{1}{c} = \frac{1}{c_0} + kt, \tag{4}$$

where c_0 is the initial concentration, 0.75. Using the value [22] of k for bulk solid H_2, the concentration should fall by a factor of two in 3.1 days. The observed conversion rate is thus in reasonable accord with that of bulk solid H_2. We note that any re-conversion during the warm-up of the sample could explain the slightly smaller apparent rate of conversion.

Neutron scattering measurements were performed on the Fermi–Chopper time-of-flight spectrometer at the NIST Center for Neutron Research using an incident neutron wavelength of 4.8 Å. The neutron-energy-gain spectrum of Dow/BNL AlH_3 powder at 3.5 K appears in Fig. 5. Because the temperature is very low compared to the energy gains involved (recall that 14.7 meV corresponds to the 171 K energy difference between the unperturbed $J=0$ and $J=1$ states), the background scattering is extremely small. The only excited states available to produce neutron-energy-gain are *ortho*-H_2 molecules, which are all $J=1$ at this temperature. The data of Fig. 5 required 16 h for each spectrum, due to the weak $J=1$:$J=0$ transition probability [26].

The Dow/BNL sample shows a relatively sharp scattering peak near 14.0 meV, reflecting H_2 molecules with energy levels similar to that of bulk H_2. This peak is consistent with what is observed from H_2 bubbles in electrochemically charged Al metal [27]. There is around a sixfold larger integrated intensity from H_2 molecules with substantially smaller $J=1$:$J=0$ energy differences. These "non-bulk" H_2 molecules behave as confined, hindered rotors [22,26] and are either isolated molecules or very small nano-clusters situated near internal cavity surfaces

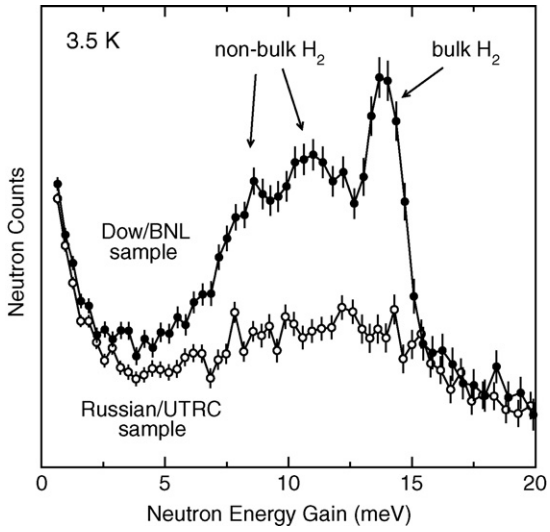

Fig. 5. Neutron-energy-gain spectra from two AlH_3 samples at 3.5 K. For the Dow/BNL sample, bulk-like H_2 molecules are apparent from the 14.0 meV scattering peak, which is near the 14.7 meV the free-rotor energy of the $J=1$ (*ortho*) to $J=0$ (*para*) transition. In contrast, the Russian/UTRC sample shows no evidence of bulk-like H_2 being present and has a much lower "non-bulk-like H_2" content.

and experiencing large crystal fields. They may also be responsible for the gradual decrease observed in normalized NMR intensity, MT. A second neutron spectrum of the Dow/BNL sample measured after 1.5 days at 3.5 K showed a similar shape but with an approximate 50% reduction in intensity indicating *ortho–para* conversion. The neutron spectrum in Fig. 5 from the Russian/UTRC sample shows no evidence of "bulk" H_2 molecules although some "non-bulk" H_2 contributes to the weak, broad peak seen above background level. However, its content is around one-third of that of the Dow/BNL sample.

From the relationship between H_2 gas pressure and proton spin-lattice relaxation times (T_1) established by Lipsicas and Hartland [28], the nominal T_1-value of 85 ms obtained at room-temperature for the narrow component in Fig. 4 implies a nominal pressure of at least ~750 bar in these bubbles. This pressure corresponds to the lower limit found for H_2 bubbles with dimensions of ~8–15 nm in heavily irradiated LiH [29]. We could not specify locations (i.e., within the bulk hydride, in or near oxide layers, etc.; ^{27}Al NMR determined Al_2O_3 should be about 8% of total aluminum) nor reliably estimate the size distribution of the bubbles in the Dow/BNL sample from the proton relaxation times or SEM images but suspect that the H_2 bubbles would be similar to those seen in Al metal [27,30]. It may be possible to determine the bubble locations and sizes via transmission electron microscopy (TEM) or small angle neutron scattering (SANS); however, such measurements were outside the scope of the present studies.

4. Conclusions

In summary, the Dow/BNL sample of AlH_3 shows a sharp NMR line with short T_1, from 423 K to below 11 K. The only species which could remain so mobile at such low temperatures is molecular H_2. Further, the H_2 must be physically trapped in the

material, possibly in cavities formed during slow decomposition, because molecular H_2 could not remain adsorbed up to 423 K. Further confirmation of the H_2 identification comes from the chemical shift value from MAS-NMR and from the observation of neutron-energy-gain peaks near the 14.7 meV (unperturbed) $J = 1$:$J = 0$ transition. The observation of *ortho–para* conversion in the NMR and neutron spectra provide still more evidence that the responsible species is H_2. We note that the H_2 energy levels may be substantially different than in bulk solid H_2, as indicated by the gradual freeze-out of normalized NMR signal intensity MT and by the broad non-bulk peak in the neutron spectrum. The α-AlH_3 material from the Russian/UTRC source shows neither NMR nor neutron scattering evidence of bulk molecular hydrogen. Proton static and MAS spectra have also been obtained on numerous freshly prepared (i.e., aged from a few days to weeks) batches of different AlH_3 polymorphs from U. Hawaii, Institute for Energy Technology (Norway) and BNL. Initially, the proton spectra of these samples did not indicate any sharp "H_2" peaks [15,16]. However, MAS-NMR indicated concurrent formation of Al metal and H_2 gas (with a shift at 4.4 ppm) from the more unstable β and γ phases with time or heating [16]. From the serial acknowledgments in Refs. [6,7] to the paper by Baranowski and Tkacz [31] who cited their source of AlH_3 material as being provided by J.J. Reilly at BNL, the lot of Dow/BNL AlH_3 studied in the present work is the same as used by Zogal et al. [6,7] when they observed the sharp "H_2" peak in their NMR spectra. In contrast to the supposition made by Zogal et al. [7] that this hydrogen is adsorbed on particle surfaces, we believe the preponderance of experimental evidence is more consistent with the H_2 molecules trapped within high pressure (i.e., ≥750 bar) bubbles for this lot of AlH_3 made by Dow.

In closing, we note that other hydrogen-storage materials (e.g., such as $NaAlH_4$) have been reported [8–14] to show similar sharp NMR peaks. While we suspect that trapped molecular H_2 may also be present in some of these materials, the peak could arise from residual solvents. However, the proton chemical shifts of these solvents are not at ∼4.4 ppm [15]. In any particular material, experiments similar to those reported here would be required for unambiguous identification.

Acknowledgments

The authors gratefully acknowledge research support (at WU) from NSF grant DMR-0400512 and (at WU and Caltech) from DOE Basic Energy Sciences grant DE-FG02-05ER46256. The NMR facility (SH) at Caltech is supported by NSF award 9724240 and partially by the NSF MRSEC program with award DMR-0520565. This work was also partially supported by DOE through EERE Grants No. DE-AI-01-05EE11104 (NIST) and DE-AI-01-06EE11105 (JPL) and BES Grant No. DE-FG02-98ER45701 (NIST), and was partially performed at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautical and Space Administration. The authors thank J.G. Kulleck for the X-ray diffraction and SEM measurements at JPL. The sources of the samples are appreciated: J. Reilly and J. Graetz at Brookhaven National Laboratory and X. Tang, D. Mosher, and S. Opalka at UTRC.

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